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EVALUATION OF ATMOSPHERIC RELEASE
TECHNIQUES FOR ATOMIC URANIUM AND
THORIUM

M. Camac, et al

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Because certain simple uranium and thorium oxides exhibit ionization potentials which are lower than their metal-oxygen bond strengths their low temperature and pressure chemistry can result in the production of stable ionized species. Release of uranium or thorium vapor in the presence of ambient atomic and molecular oxygen in the upper atmosphere may result in the formation of stable ionic metal clouds which extend over large volumes. Radar and optical observation of these clouds could yield information

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about upper atmospheric properties.

This report reviews a number of techniques for the release of U and Th which may be adaptable to field experimental conditions. The techniques reviewed include the release of volatile compounds containing U and Th, evaporation by chemical and electrical heating, and exploding wires.

EVALUATION OF ATMOSPHERIC TECHNIQUES FOR ATOMIC URANIUM THORIUM

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FOREWORD

This technical report was prepared under Contract F30602-73-C-0162, ARPA Order No. 1649 by Aerodyne Research, Incorporated, Tech/Ops building, Northwest Industrial Park, Burlington, MA 01803.

This technical report has been reviewed and is approved.

RADC Project Engineer

ABSTRACT

Because certain simple uranium and thorium oxides exhibit ionization potentials which are lower than their metal-oxygen bond strengths their low temperature and pressure chemistry can result in the production of stable ionized species. Release of uranium or thorium vapor in the presence of ambient atomic and molecular oxygen in the upper atmosphere may result in the formation of stable ionic metal clouds which extend over large volumes. Radar and optical observation of these clouds could yield information about upper atmospheric properties.

This report reviews a number of techniques for the release of U and Th which may be adaptable to field experimental conditions. The techniques reviewed include the release of volatile compounds containing U and Th, evaporation by chemical and electrical heating, and exploding wires.

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INTRODUCTION

Recent laboratory experiments have shown that uranium's oxidation chemistry at room temperature exhibits unusual properties. Simple uranium oxide ions which are stable at low densities can be produced in a mixture of uranium atoms and oxygen. Consequently, it has been speculated that the release of uranium in the upper atmosphere (above ~100 km) could furnish a mechanism for studying some properties of the upper atmosphere.[1] Release of uranium atoms or ions may result in the formation of stable ionic uranium oxide clouds which extend over large volumes. There is no requirement for sunlight to produce ionization as in the case of the barium releases. Thus radar and optical observations could be made of ion clouds during both night and day. The optical radiation from these clouds would be mainly scattered earthshine in the infrared or scattered visible and near infrared radiation from the sun. These ionic oxides should persist for many minutes at altitudes above 100 km, where three-body collisions are infrequent. While less is known about the oxidation chemistry of thorium, it should be qualitatively similar to that of uranium.

This paper explores methods for releasing uranium and thorium vapors in the upper atmosphere. The same methods would apply to releases of other metals, such as iron and aluminum; however, the extension to other metals is not considered. Among the techniques treated is the release of gaseous compounds that contain uranium or thorium which would decompose or react in the upper atmosphere to form simple oxides. Evaporative deposition based on several thermochemical heating schemes is discussed. Several electrical heating schemes are also considered, including electron beam bombardment and resistive heating oxidation processes that heat metal coated surfaces, and exploding wires. An important output of this study is the weight of the released metal compared to the weight of the entire system. The maximum ratio of metal would be obtained with gaseous releases. The metal evaporation method would require much more weight, but it has the advantage of releasing a pure substance for which one might develop theoretical predictions of the chemistry.

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1. POSSIBLE URANIUM AND THORIUM COMPOUNDS FOR USE IN HIGH-ALTITUDE GASEOUS RELEASE EXPERIMENTS

C.E. Kolb

INTRODUCTION

The releasing of rocket-borne volatile compounds has been established as a useful method for determining metal-atom and metal-oxide chemistry in the oxygen-atom-rich upper atmosphere between altitudes of 90 and 250 km. Successful releases of trimethyl aluminum,[1-1, 1-2] diborane,[1-3] and iron carbonyl[1-4] have been reported to date.

This section identifies possible classes of uranium and thorium containing volatile compounds that could be oxidized by atmospheric O and O_2 to produce either free metal atoms or metal oxides. Candidate compounds were judged for their having a vapor pressure of 1.0 Torr without extensive decomposition at temperatures below $1000^{O}K$. The criteria for producing only metal atoms and oxides were used to rule out compounds with metal-halogen and metal-nitrogen bonds (e.g., UF_6). But uranyl compounds with the form $UO_2(X)_n$ were explored, primarily because they cannot be expected to yield either free U or UO in release experiments. The data identified as sublimation temperatures in this review merely reflect points where the compounds can be purified with vacuum sublimation techniques and may indicate vapor pressures of no more than 10^{-4} Torr.

COMPOUND TYPES

1.1 Biscyclooctatetraenyl Uranium and Thorium
(Uranocene and Thoracene), $U(C_8H_8)_2$ and $Th(C_8H_8)_2$

Compound	Molecular Weight	Sublimation Temp. (^{O}C)	Decomposition Temp. (^{O}C)
$U(C_8H_8)_2$	446	180	---
$Th(C_8H_8)_2$	440	160	190

1

Comments

Both compounds have π-ring-actinide f-orbital sandwich-type structures, and both were synthesized recently by Streitweiser.[1-5, 1-6] Each compound is air sensitive: uranocene enflames in air, but is stable in water; thoracene decomposes in water and air, but does not burn spontaneously. Little detailed data are available about vapor pressure, but uranocene is reported to have a vapor pressure of 0.03 Torr at 180°C. While thoracene can be vacuum sublimed at 160°C, it decomposes without melting at 190°C, and explodes if heated red-hot. No decomposition temperature for uranocene has been reported; Streitwieser terms it thermally stable.[1-5]

It seems possible that uranocene may develop sufficient vapor pressure ($\sim$10 Torr) at some point below its decomposition temperature to be useful as a release chemical.

1.2 Uranium and Thorium Tetrakishydroborate, $U(BH_4)_4$ and $Th(BH_4)_4$, and derivatives

Compound	Molecular Weight	Melting Point (°C)	Sublimation Temp. (°C)	Decomposition Temp. (°C)
$U(BH_4)_4$	297	---	30	100
$Th(BH_4)_4$	291	203	---	300
$U(BH_4)_3(BH_3CH_3)$	311	85-95	---	---
$U(BH_3CH_3)_4$	353	72-74	---	---

Comments

These compounds, which are formed with eight three-center (M-H-B) bridging hydrogen bonds each (no metal-boron bonds), have recently been reviewed by James and Wallbridge.[1-7] Each compound hydrolyzes slowly in air. $Th(BH_4)_4$ decomposes at 300°C to ThB_4, while $U(BH_4)_4$ decomposes at 100°C to form a $U(BH_4)_3$ polymer. The vapor pressure of $Th(BH_4)_4$ has been reported at 0.2 Torr at 150°C, and its enthalpy of vaporization is estimated at 21 kcal/mole.

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$U(BH_4)_4$ was first synthesized by Schlesinger and co-workers,[1-9] who made detailed sublimation pressure measurements and derived the following empirical relationship between the temperature and vapor pressure of $U(BH_4)_4$:

$$\text{Log } P_{Torr} = -4,265/T(^{O}K) + 13.354 \quad .$$

This relationship was compared to measured vapor pressure as shown below:

Temperature (^{O}C)	34.2	40.2	48.2	54.2	61.3
P_{obs}(Torr)	0.30	0.56	1.23	2.15	4.00
P_{calc}(Torr)	0.30	0.56	1.20	2.12	3.98

They also report a vapor pressure of 13.86 Torr at a temperature of $79^{O}C$ in a description of a molecular weight determination.

Schlesinger and co-workers also reported the synthesis of two methyl derivatives of $U(BH_4)_4$: $U(BH_4)_3(BH_3CH_3)$, and $U(BH_3CH_3)_4$. They found that the monomethyl derivative $U(BH_4)_3(BH_3CH_3)$ is more volatile than $U(BH_4)_4$, with its vapor pressure represented by the following empirical relationship:

$$\text{Log } P_{Torr} = -3,160/T(^{O}K) + 10.500 \quad ,$$

based on the following data:

Temperature (^{O}C)	25.1	31.4	38.1	45.4	50.7	58.0	65.6
P_{obs}(Torr)	1.06	2.13	3.37	5.56	8.52	14.6	25.8
P_{calc}(Torr)	1.24	2.05	3.44	5.87	8.53	14.0	23.4

A similar relationship for the tetramethyl derivative was

$$\text{Log } P_{Torr} = -2,960/T(^{O}K) + 8.815 \quad ,$$

which yields a vapor pressure of about 1.9 Torr at $73.7^{O}C$.

1.3 Uranium and Thorium Cyclopentadienide Compounds

In a recent review of the organo-metallic compounds of the lanthanides and actinides, Hayse and Thomas[1-10] identified a number of volatile uranium and thorium compounds in which the cyclopentadienide group,(C_5H_5), is the primary ligand. A number of these, with available physical data, are listed in this section.

1.3.1 Uranium tricyclopentadienide, $U(C_5H_5)_3$

Compound	Molecular Weight	Sublimation Temp. (^{O}C)	Decomposition Temp. (^{O}C)
$U(C_5H_5)_3$	433	120-150	> 200

Comments

This compound is air and moisture sensitive, but apparently quite stable thermally. The thorium analog is apparently unstable and has not been synthesized, although Pu, Am, Cm, Bu, and Cf analogs have been synthesized.

1.3.2 Uranium tricyclopentadienide hydroboride, $U(C_5H_5)_3BH_4$

Compound	Molecular Weight	Sublimation Temp. (^{O}C)
$U(C_5H_5)_3BH_4$	448	170

Comments

Little physical data has been reported on this compound -- synthesized by Anderson and Crisler.[1-11] The thorium analog has not yet been made. The vapor pressure at 170^OC is 10^{-4} Torr.

1.3.3 Uranium and thorium tricyclopentadienidealkoxides,

$U(C_5H_5)_3 OCH_3$ and $Th(C_5H_5)_3 OCH_3$ (methoxides)
and

$U(C_5H_5)_3 OC_4H_9$ and $Th(C_5H_5)_3 OC_4H_9$ (n-butoxides)

4

Compound	Molecular Weight	Melting Point ($^{\circ}$C)	Sublimation Temp. ($^{\circ}$C)
$U(C_5H_5)_3OCH_3$	464	---	~ 120 (vp = 10^{-4} Torr)
$Th(C_5H_5)_3OCH_3$	458	---	$\simeq$ 135
$U(C_5H_5)OC_4H_9$	506	148-150	---
$Th(C_5H_5)_3OC_4H_9$	500	148-150	---

Comments

In their report on these compounds, Ter Haar and Dubeck[1-12] stated that the n-butoxides melt while the methoxides darkened without melting over a wide temperature range. There appears to be some chance that the butoxides would develop sufficient vapor pressure for releases. In addition, other more volatile tricyclopentadienide alkoxides could probably be synthesized. Note that these compounds have one M-O atom bond.

1.3.4 Uranium and thorium tetracyclopentadienide, $U(C_5H_5)_4$ and $Th(C_5H_5)_4$

Compound	Molecular Weight	Decomposition Temp. ($^{\circ}$C)
$U(C_5H_5)_4$	498	250
$Th(C_5H_5)_4$	492	170

Comments

No vapor-pressure data for these compounds are available.

1.4 Uranium and Thorium 1,3-β-dicarbonyls, $U(RCOCH_2COR')_4$, $Th(RCOCH_2COR')_4$

A large number of uranium chelate compounds of this family were prepared by Schlesinger and co-workers at Chicago,[1-13] and by Gilman and co-workers at Iowa State[1-14] during World War II when great effort was expended in searching for volatile uranium compounds. Approximately 30 of these compounds were prepared with such R and R' groups as CH_3, C_2H_5, C_3H_7, C_6H_5, C_4H_9, CF_3, OCH_3, OC_2H_5, and OC_4H_9.

Most of these compounds are either liquids at room temperature, or melt below $200^{\circ}C$. Many also boil below $200^{\circ}C$. Unfortunately, they all are quite temperature sensitive and decompose extensively before generating vapor pressures much above 0.1 Torr. Details on synthesis, melting and boiling points, and available vapor pressure measurements on these compounds are found in References (1-13) and (1-14). It should be noted that Schlesinger stopped work on this type of compound after $U(BH_4)_4$ was successfully synthesized.

Although the synthesis and melting points of a number of thorium dicarbonyls were reported by Wolf and Jahn, [1-15, 1-16] little data are available from vapor pressure measurements. The most work has been done on thorium acetylacetonate, $Th(C_5H_7O_2)_4$, for which Young[1-17] measured a vapor pressure of 3.2×10^{-4} Torr at $100^{\circ}C$. This compound boils at 260 to $270^{\circ}C$ at 1-atmosphere pressure, but extensive decomposition occurs.

Since this class of chelates coordinates through U ... O=C linkages, release might lead to such highly oxygenated compounds as UO_2, rather than to free U or even to UO.

1.5 Thorium and Uranium Alkoxides,

$Th(OR)_4$, and $U(OR)_5$ and $U(OR)_6$, and derivatives

Uranium tetra-alkoxide compounds, $U(OR)_4$, are not so well characterized or so volatile as the pentalkoxides. Pentamethoxide, $U(OCH_3)_5$, is a solid crystal at room temperature and trimeric in solution, but higher oxides are more volatile. For instance, the pentaethoxide -- $U(OC_2H_5)_5$, penta-1-propoxide -- $U(OC_3H_7)_5$, penta-1-butoxide -- $U(OC_5H_9)_5$, and penta-1-pentoxide -- $U(OC_5H_{11})_5$ are volatile liquids and dimeric in solution.[1-18] The pentaalkoxides were prepared by Bradley and co-workers, [1-19, 1-20] while Jones, et al., [1-21] reported a number of volatile substituted derivatives of the pentaalkoxides.

Some characteristic compounds with available physical data are listed here, but no detailed vapor-pressure data appear to have been published.

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Compound	Melting Point ($^{\circ}$C)	Boiling Point ($^{\circ}$C)
$U(OC_2H_5)_5$	< 30	< 140-160 at 0.05 Torr
$U(OC_3H_7)_5$	< 30	< 150 at 0.05 "
$U(OCH_2CF_3)_5 \cdot (CH_3)_2CHNH_2$		100-103 at 0.01 "
$U(OCH_2CF_3)_5 \cdot 2(CH_3)_3N$	< 30	95-100 at 0.02 "
$U(OC_2H_5)_3(CF_3COCHCO_2C_2H_5)_2$		100-105 at 0.004 "

Jones and co-workers[1-22] also reported on $U(OCH_3)_6$, $U(OC_2H_5)_6$, and $U(OC_3H_7)_6$. These compounds and their physical properties are listed below.

Compound	Melting Point ($^{\circ}$C)	Boiling Point ($^{\circ}$C)
$U(OCH_3)_6$	< 30	72-74 at 0.001 Torr
$U(OC_2H_5)_6$	< 30	96-98 at 0.001 "
$U(iso-OC_3H_7)_6$	167-168	--- -
$U(n-OC_3H_7)_6$	< 30	115° at 0.004 Torr

Jones, et al., noted that these U(VI) alkoxides are all unstable to heat.

A number of thorium tetraalkoxides have also been reported by Bradley and co-workers. [1-23, 1-24] The simplest of these compounds, the methoxide, $Th(OCH_3)_4$, is a highly polymerized white solid, but the degree of polymerization is reduced, and compound volatility is increased as the alkoxide ligand increases in complexity. Several of the more volatile compounds and their boiling points are indicated below.

-R in Th(OR)$_4$	Boiling Point ($^{\circ}$C)
$-C(CH_3)_3$	160 at 0.1 Torr
$-C(CH_3)_2(C_2H_5)$	208 at 0.3 "
$-C(C_2H_5)_2(CH_3)$	148 at 0.1 "
$-C(C_2H_5)_3$	148 at 0.05 "
$-C(CH_3)(C_2H_5)(n-C_3H_7)$	153 at 0.1 "
$-C(CH_3)(C_2H_5)(t-C_3H_7)$	139 at 0.05 "

As in the case of the β-dicarbonyl compounds, the alkoxides have direct M-O bonds, and probably will not directly produce either free metal atoms or metal monoxides in the upper atmospheric release environment.

SUMMARY

From the rather scant data in the literature, it appears that the tetrakishydroborate compounds (and their methyl derivatives) of uranium and thorium are the most suitable substances for the formation of U or Th atoms and simple oxides in upper atmospheric releases. Published work on diborane releases[1-3] indicate that the BH_4 ligands oxidize to BO_2 and H_2O. However, additional data are needed to rule out the possibility of U-B bond formation in the release environment. Among the organo-metallic compound types that contain only M, C, and H atoms, uranocene and thorocene most warrant further study.

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2. INVESTIGATIONS OF URANIUM EVAPORATION BY THERMOCHEMICAL HEATING

B. W. Worster

INTRODUCTION

It is desired to devise methods of evaporating metallic uranium at vacuum-expansion altitudes without releasing other species in the process. This section summarizes studies of two systems that burn a substance (carbon or magnesium) in the presence of oxygen within a closed container. The first criterion for the system to function is for the exterior of the container to be heated to sufficient temperature to evaporate U_{238} ($\sim 3100^{O}$K). For flyable systems, such other factors as weight and material properties are also important. Design details for the two systems considered here are listed in Table II.

TABLE II
THERMOCHEMICAL FLASH HEATING

	Carbon/Oxygen System	Magnesium/Oxygen System
Dimensions	Cylinder	Spherical Shell

	Length 50 cm
	OD 1.2 cm
	ID 1.0 cm
	Surface 188 cm
	  Area
		Diameter 8 cm
		Thickness 0.5 cm
		Surface 200 cm^2
		  Area

Burn Duration	$\sim$1 sec	$\sim$1 sec
Fuel Consumed	12 g Carbon	12.3 g Magnesium
Oxygen Consumed	16 g (12 atm-liters)	8.1 g (8.5 atm-liters)

Combustion Products	23 atm-liters CO
	  (Gaseous)
		6 cm^3 MgO
		  (Condensed)

External Surface Temperature	$\sim 2500^{O}$K (Maximum)	$\sim 3200^{O}$K
Heat Loss	3.4 kcal/sec	13.8 kcal/sec
Amount of U_{238} Evaporated	Negligible	11 g
System Weight	$\sim$ 50 lb	$\sim$ 25 lb

CARBON COMBUSTION SYSTEM

The first system investigated is shown in Fig. 2.1. A hollow graphite tube is coated with hafnium carbide (the best high-temperature ceramic available), and is plated with the U_{238} to be evaporated. Oxygen is inserted under pressure from one end of the tube and interacts at the wall via surface reaction to form carbon monoxide. The walls are heated in the process, and the CO is removed by an absorption pump.

However, this system fails to achieve a sufficient temperature because a substantial fraction of the original tube thickness must remain to withstand the pressures produced by the reaction, and the heat capacity of graphite is such that the energy available is insufficient to raise the tube to the necessary temperature. (The system appears to limit at roughly $2500^{\circ}K$.)
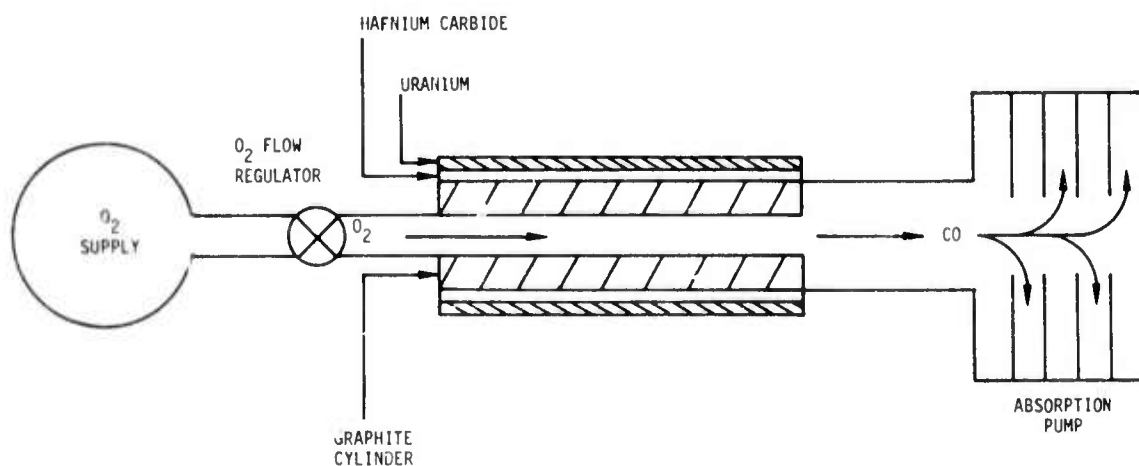

Fig. 2.1. Carbon/Oxygen System.

MAGNESIUM FLASH EVAPORATOR

The magnesium flash evaporator evaporates uranium (or thorium) from the exterior surface of a thin spherical shell of hafnium carbide. Heat for this process is generated within the shell by the flash burning of magnesium in the presence of oxygen. None of the heat produced is carried out of the shell by gaseous by-products.

Figure 2.2 shows the cross-sectional details of a prototype system. The reaction

$$Mg + \frac{1}{2} O_2 \rightarrow MgO$$
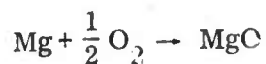
is used because very little heat is released by the production of gaseous MgO. However, upon condensation to liquid or solid MgO, a large amount of heat is produced. If the shell is heated to $3300^\circ K$ and the outside to $3200^\circ K$ the MgO can still condense to a liquid on the shell's inner surface and release 88 kcal/mole. Furthermore, the low-vapor pressure of MgO means the interior pressure of the shell will be a function of only the oxygen consummation rate and O_2 temperature.
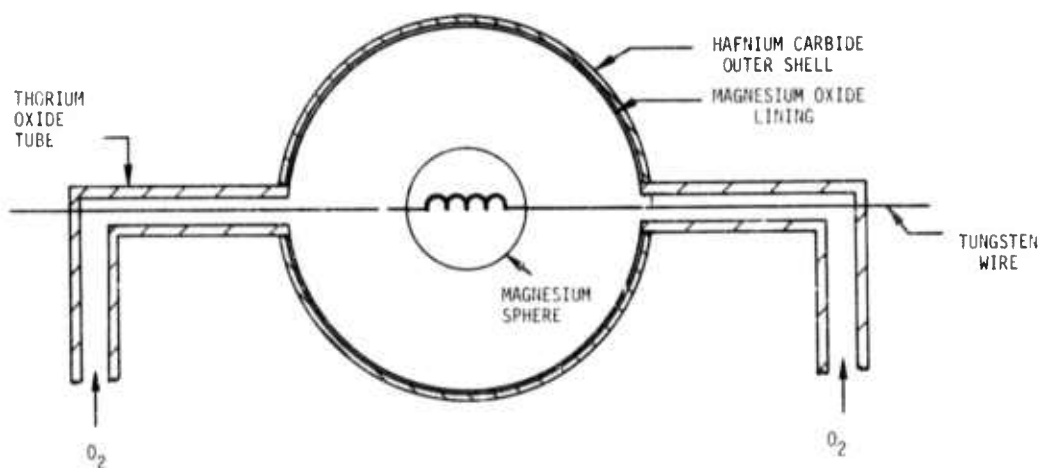

Fig. 2.2. Magnesium/Oxygen System.

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Operation of the evaporator is as follows: initially, the shell contains some oxygen. The magnesium forms a sphere at the center of the shell. The shell is initially lined with some MgO to protect the HfC from the O_2 (and, possibly, from the Mg vapor). Electrical current passed through the tungsten wire is used to heat the magnesium surface above its ignition point. The magnesium ignites, vaporizing more Mg from the surface of the shell, and the Mg burns to MgO as more oxygen enters. The MgO condenses on the hafnium carbide walls and heats them. This heat evaporates the uranium on the exterior, and the thorium oxide tubes are cooled by the incoming oxygen. Even if the shell should rupture from thermal stress, the complete burning of the magnesium will cause no pressure dispersion of the fragments and no gaseous by-products (except for traces of residual Mg and O_2 vapor).

Parameters for a typical system, allowing for thermal capacity of materials and radiative heat losses, are as follows:

Burn Duration	1 sec
Uranium Evaporated	11 g (0.058 g/cm^2-sec)
Surface Area	200 cm^2 (8-cm diameter)
Shell Thickness	0.5 mm
Magnesium	12.3 g
Oxygen	8.1 g (8.5 atm-liters)
External Surface Temperature	3100°K
Combined Radiative and Evaporative Heat Loss	13.8 kcal/sec (0.069 kcal/cm^2-sec)
Volume of MgO Produced	6 cc.

If a larger quantity of uranium or a higher temperature (for thorium) is required, the diameter, burn time, and burn rate of the system can be adjusted accordingly.

Based on the sizes of typical hardware, the weight of a flyable package, including electrical ignition equipment and oxygen storage, could easily be kept with 25 pounds.

This system might still be unworkable if other factors prove unfavorable. The first item is the internal pressure of the device. This is a function of the mechanism and the burning rate of magnesium, which appears to be a combination of gas-phase and surface reactions, and which is unmeasured at pressures ~1 atm. [2-1, 2-2, 2-3]

The vapor pressure of MgO at these temperatures has not been measured. If the vapor pressure is sufficiently low to raise the possibility that the MgO goes quickly to the condensed state, then it is possible that the internal pressure will remain low -- with the incoming oxygen and the evaporating Mg being consumed as fast as they appear. In fact, under optimum conditions, the device may act as an absorption pump for the O_2. The 100^OK temperature drop across the HfC shell is based on thermal conductivities of similar ceramics at lower temperatures, and must be measured to determine the feasibility of the system. The tensile strength of hafnium carbide is also a factor. A ceramic with similar properties, ZrC, gains in tensile strength between 1250 and 1470^OK, and is sufficiently strong for the geometry discussed here to withstand 10 atm,[2-4] but the tensile strength of neither ceramic is known at 3200^OK. All in all, a variety of properties of the materials must be evaluated before the final workability of this concept can be determined.

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3. ELECTRONIC HEATING TECHNIQUES FOR METAL VAPOR RELEASES

R.C. Sepucha

INTRODUCTION

The vapor pressures[3-1] of uranium and thorium are plotted in Fig. 3.1 as functions of temperature. The relatively low values of the pressures require that evaporation of these metals occur at temperatures above 3000°K to ensure substantial production of the vapor in heating times on the order of ten seconds. This high operating temperature, coupled with the weight and power restrictions of flight experiments, limits the types of vaporization schemes that may be employed.

Heating of a surface coated with uranium or thorium can be accomplished by resistance (ohmic) heating or electron-beam heating, the apparatus for which is shown schematically in Fig. 3.2. In the first case, a dc voltage directly heats an element coated with the metal to be evaporated. In the second case, the heated element emits electrons which in turn heat the surface of a coated anode. In both cases, the temperature of the coated element can be controlled by varying the applied voltage or current. The power applied to the element is dissipated by radiation, for which the heat loss is

$$Q_R = \epsilon \sigma T^4 = 1.89 \left(\frac{T}{1000} \right)^4 \frac{\text{watts}}{\text{cm}^2} \quad , \tag{3-1}$$

and by evaporation of the surface, for which the heat loss is

$$Q_E = \frac{\epsilon_v p}{\left(2\pi MkTN_o \right)^{1/2}} = \frac{257 \, \epsilon_v p}{\sqrt{TM}} \frac{\text{watts}}{\text{cm}^2} \quad . \tag{3-2}$$

In these expressions, T is the temperature, p is the vapor pressure in Torr, ϵ is the spectral emissivity taken to be 0.33, σ is the Stefan-Boltzmann constant, ϵ_v is the heat of vaporization in kcal/mole, M is the molecular weight, k is the Boltzmann
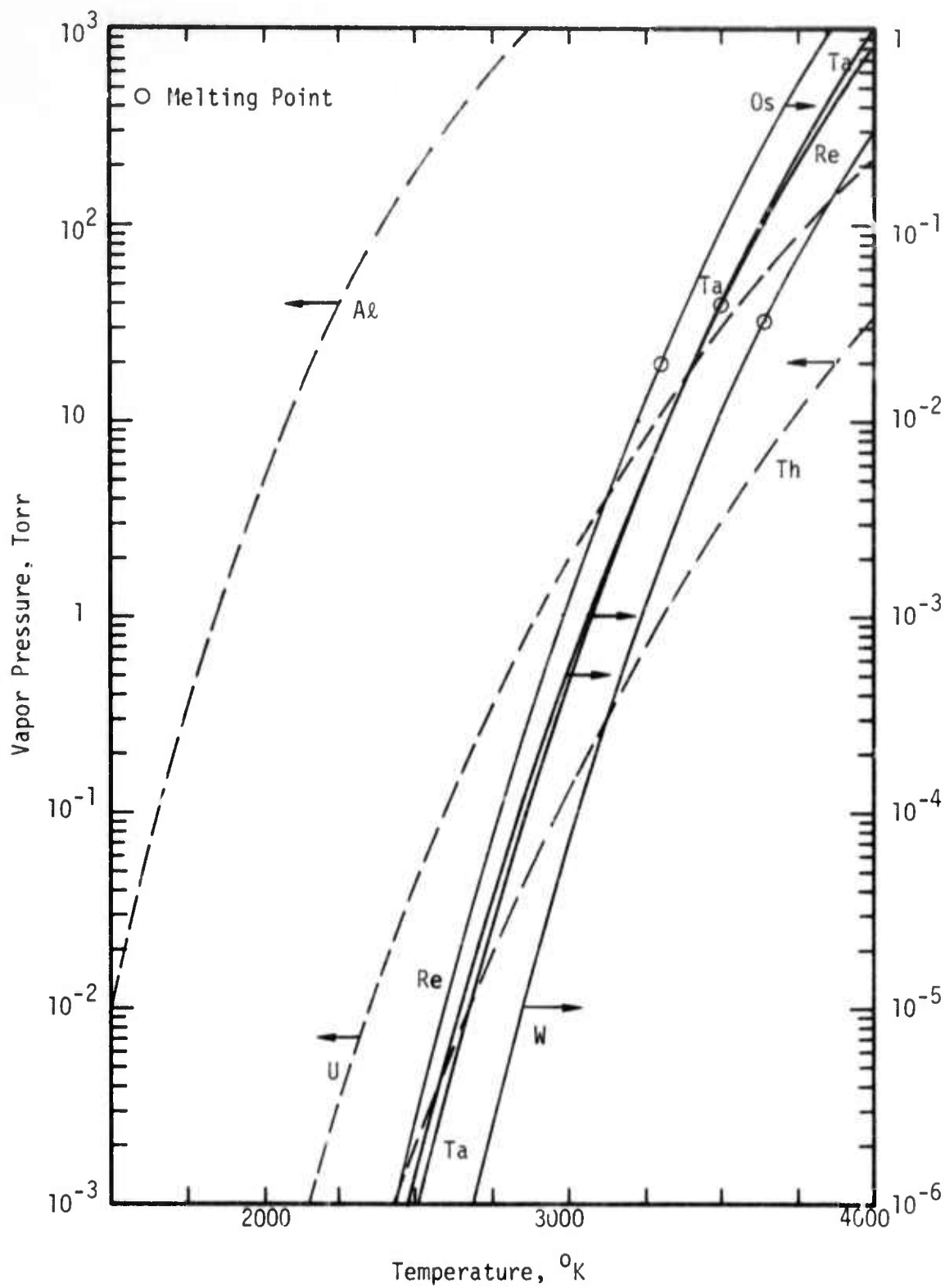
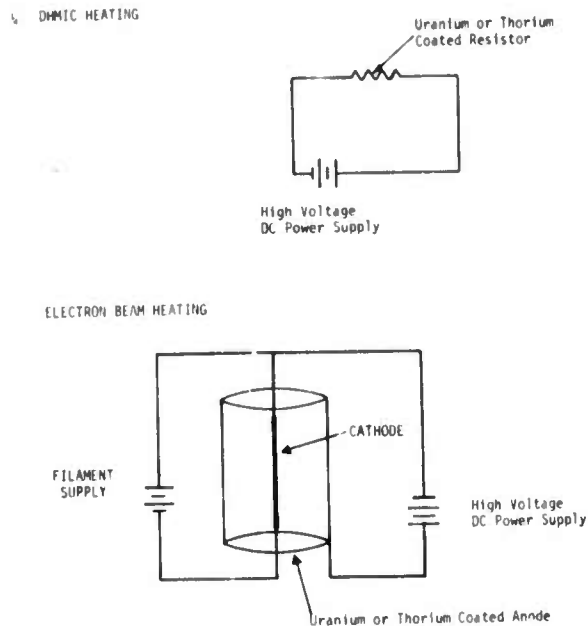Fig. 3.1. Vapor Pressure of Solid Elements.[3-1]

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Fig. 3.2. Metal Evaporation by Electric Heating.

constant, and N_0 is Avogadro's number. The evaporation rate, dm/dt, is given by

$$\frac{dm}{dt} = p \left(\frac{M}{2\pi k T N_0} \right)^{1/2} = 6.1 \times 10^{-2} \ p \left(\frac{M}{T} \right)^{1/2} \frac{gm}{cm^2\text{-sec}} \quad , \tag{3-3}$$

so that

$$Q_E = 4.18 \times 10^3 \left(\frac{\epsilon_v}{M} \right) \frac{dm}{dt} \quad \frac{watts}{cm^2} \quad . \tag{3-4}$$

Equations (3-1) and (3-2) are plotted in Fig. 3.3 as functions of temperature for aluminum, iron, uranium, and thorium. For the last two metals, evaporation is the dominant cooling process above 3200° and 3650°K, respectively.
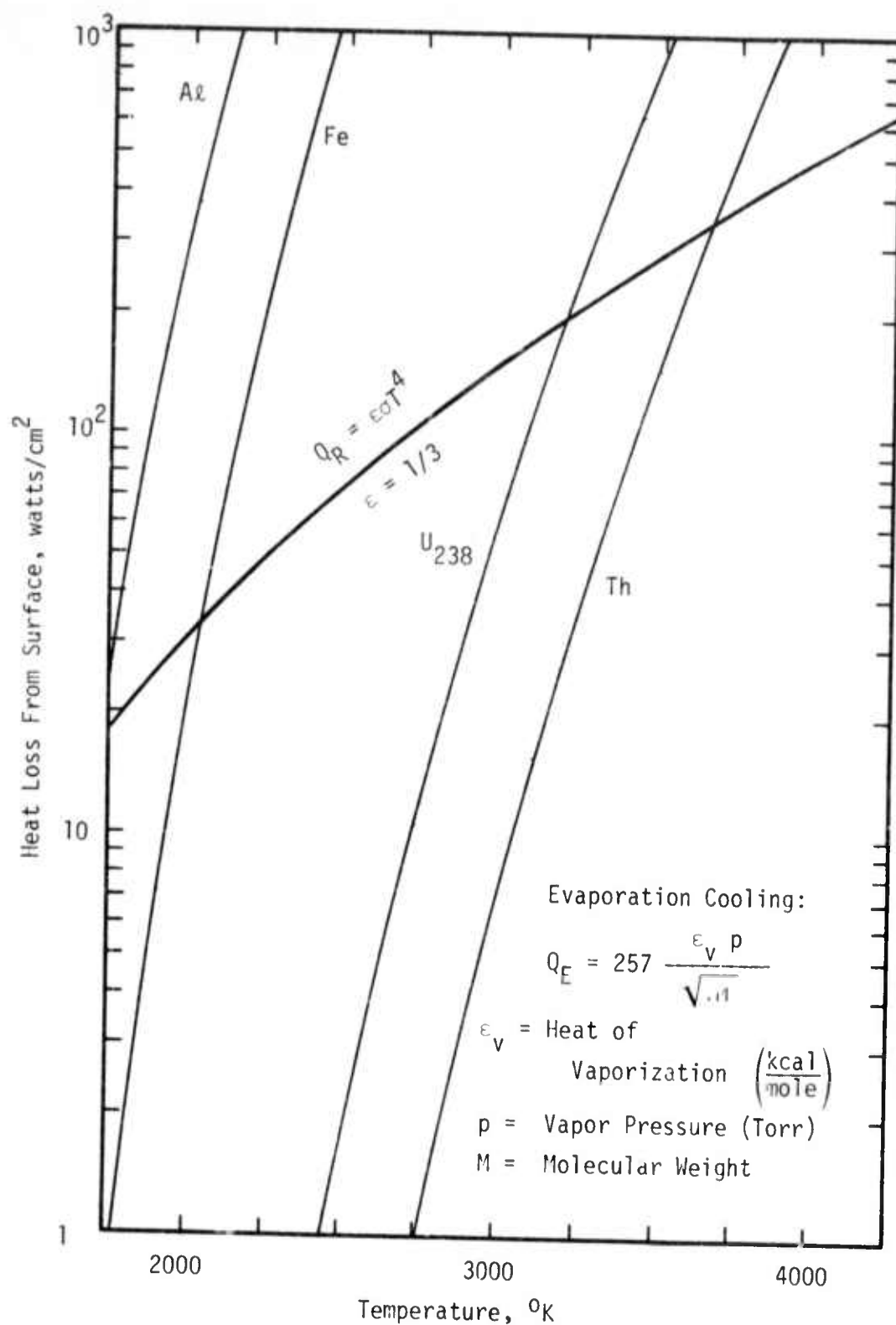
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Fig. 3.3. Comparison of Surface Cooling by Radiation and Evaporation.

Based on Eqs. (3-1) through (3-4), the rate of metal evaporation by constant temperature electrical heating is shown plotted in Figs. 3.4 and 3.5 as a function of electrical power input for uranium and thorium, respectively. For each case, the highest temperature indicated is that at which the cooling rate due to evaporation is equal to that due to radiation. For uranium, 50 kW of electrical power is sufficient to evaporate approximately 25 g/sec, given a surface area of 250 cm^2 In this case, evaporation occurs at 3200^OK, the temperature being higher for smaller surface areas. For thorium at the same power input, the evaporation rate is 17 g/sec for a 160 cm^2 surface area heated to 3650^OK.

Thermal batteries producing 50 kW (5000V, 10A) for 10 seconds on a nonrecurring basis, and weighing on the order of 75 lbs, fall within the present state of the art. Therefore, the evaporation of substantial amounts of uranium and thorium is feasible for flight applications by this technique. The metal-vapor-to-electrical-system weight ratio is 0.7% for uranium and 0.5% for thorium.

The principal difficulty in both heating configurations is the compatibility of uranium with the substructure of the heating element. Intergranular penetration appears to be the mechanism that makes most substances porous to uranium at high temperatures.[3-2] Of the group consisting of titanium, zirconium, molybdenum, niobium, tungsten, and tantalum, only tungsten presents substantial resistance to penetration by uranium at the melting point of uranium (1400^OK). At temperatures above 2000^OK, the penetration problem becomes more severe and requires that tungsten be shielded from the molten uranium. Hafnium carbide appears to be a strong candidate for use as a coating material. Titanium carbide, tungsten boride, and such alloys as tungsten with hafnium or tungsten with rhenium should also be considered.

In the resistance heating method, the uranium coated wire must retain its electrical and structural integrity for approximately 10 seconds at temperatures in excess of 3000^OK. Penetration of the wire by molten uranium is tolerable, provided this does not seriously decrease the yield of uranium vapor. Similarily, in the electron-beam method, the electrical and structural integrity of the anode must be maintained, but only to the extent that the vapor yield during the heating period is not substantially decreased.
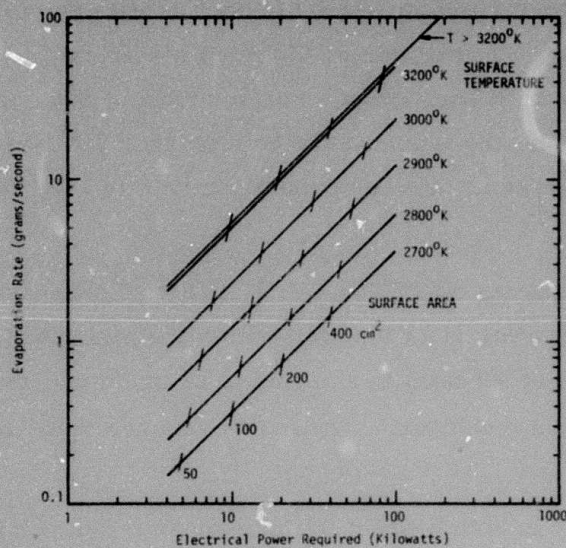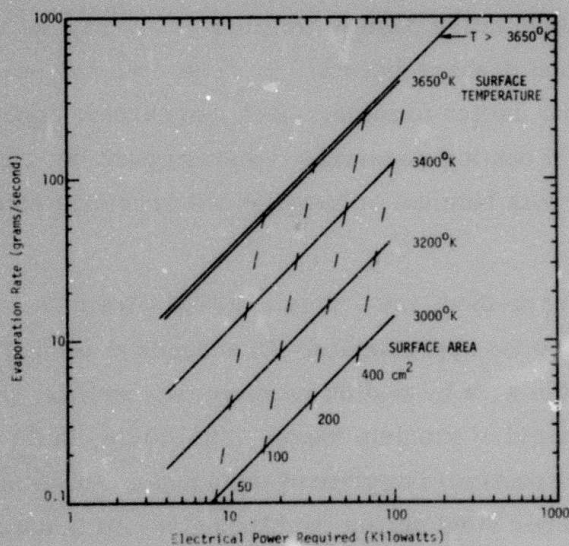
Fig. 3.4. Evaporation Rate of Uranium.

Fig. 3.5. Evaporation Rate of Thorium.

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For the resistance heating configuration, a No. 30-gauge tungsten wire 30m long, coated with, for example, hafnium carbide, with an outer coating of uranium 0.5 mm thick would be sufficient to evaporate 250 grams of uranium in 10 seconds by dissipating 50 kW of power.

Although the heating mechanisms are equivalent in the two electrical techniques, the electron-beam configuration may have some advantage over the resistance heating configuration in mechanical stability. Larger, more uniformly heated surface areas are attainable with the former, so that the system and, hence, the amount of metal vapor produced are more readily scaled to larger dimensions if the necessary power supplies become available. The electron-beam configuration would also decrease the possibility of electrical hot spots occurring that could terminate the heating process prematurely. Finally, the electron-beam technique is essentially a high-voltage, low-current method that would be more amenable to a battery-type power supply.

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4. EXPLODING WIRE TECHNIQUE FOR METAL VAPOR RELEASES

Fritz Bien

INTRODUCTION

The use of exploding wires is a technique for producing metal vapor in a relatively short time. The heating and vaporizing of the wire is typically on the order of a few microseconds, and temperatures generally rise to several times the vaporization temperature. This technique differs from the electrical heating techniques for vapor release discussed in the previous section, because the heating is nearly instantaneous, and steady-state evaporation rates do not apply.

The principal advantage in using this method (instead of electrical heating techniques) is that the wire is heated more rapidly. The energy loss due to radiation is thus low, and structural integrity of the wire at high temperatures is not necessary, since vaporization of the entire wire takes place before motion occurs. Therefore, the use of substrate materials to support the metal to be evaporated (uranium or thorium) is unnecessary.

However, one of the problems in using the exploding wire technique is the forming of a sheath of conducting plasma away from the exploding wire. This sheath may drain a large portion of the energy from the system. But this problem has been virtually eliminated by Chase, et al. [4-1, 4-2] through their use of a dielectric to encapsulate the wire.

A diagram for a typical exploding wire circuit is shown in Fig. 4.1. Electrical energy is stored in the capacitor, C, which discharges through the wire, whose resistance is R_w, and whose inductance is L_w. The current through this wire is a function of the wire resistance, which changes as the wire becomes heated, and the capacitor voltage. Since much more energy is dissipated into the wire than it can lose from
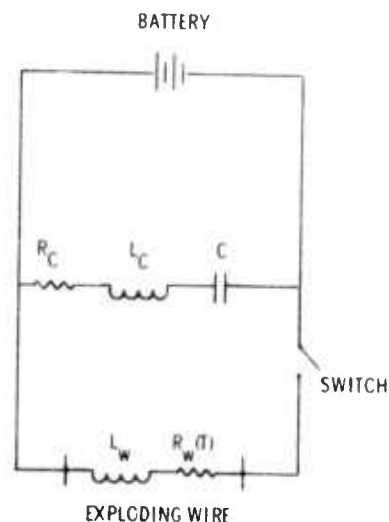

Fig. 4.1 Diagram for Simple Exploding Wire Circuit.

evaporation or radiation, the wire heats up to a very high temperature before the hot plasma can move away from the terminals holding the original exploding wire.[4-3] The energy is dissipated in five periods: During period 1, the wire is heated to melting; in the case of uranium, this includes going through several phase changes. During period 2, the wire melts and turns itself into a liquid. During period 3, the liquid keeps on heating until it reaches the vaporization temperature associated with the local pressure. This pressure is governed by the shock wave as the surface metal vapor from the wire tries to move away from the exploding wire. During period 4, the entire wire turns into vapor. Finally, during period 5, the vapor moves away from the terminals and, thus, breaks the conductivity path.

The energy equation for the wire heating is

$$C_v \Delta T = \text{Energy In} - Q_r \Delta t - \Delta m \left(H_p + H_m + H_2 \right) \quad , \tag{4-1}$$

where ΔT is the change in temperature of the wire whose specific heat is C_v, and the quantities H_p, H_m, and H_v represent the respective energies for 1) changing phase, 2) melting, and 3) vaporizing. The quantity Q_r is the energy loss rate due to radiation over the time Δt.

When neglecting the loss of energy due to radiation, the energy equation becomes

$$\text{Energy In} = 3 \times 10^{-2} \, m \Delta T + [\, 490 \text{ cal/gm}\,] \, m \tag{4-2}$$

for uranium, and

$$\text{Energy In} = 3 \times 10^{-2} \, m \Delta T + [\, 700 \text{ cal/gm}\,] \, m \tag{4-3}$$

for thorium, where m is the mass of the wire.

To obtain the energy input, the circuit equation for Fig. 4.1 is

$$L \frac{dI}{dT} + IR + \frac{1}{C} \int_0^t I \, dt = V_o \quad , \tag{4-4}$$

where I is the current through the circuit; R, the total circuit resistance, $R_L + R_w(T)$; L, the circuit inductance; C, the capacitance; and V_o, the initial voltage to which the capacitor is charged.

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With the assumption that all the energy from the capacitor goes into either heating or vaporizing the wire, the energy stored is

$$E = \frac{V_o^2}{2} C \quad .$$

(4-5)

The fraction of this stored energy that goes into the exploding wire is a function of the ringing frequency calculated from Eq. (4-4) and of the heating rate found from Eq. (4-1). This heating rate depends on 1) the diameter of the wire, 2) its length, 3) the impedance of the associated circuitry, and 4) the resistivity of the metal as a function of temperature in its liquid and vapor states.

The amount of uranium and thorium that is melted as a function of energy put into the wire is shown in Fig. 4.2. The wire is assumed to heat up to three times the vaporization temperature, as has been observed in copper and tin exploding wires. The actual temperatures that uranium and thorium reach must be determined experimentally. These temperatures have been found to be higher than the critical temperatures for the metals and dependent on the wave speed of the vapor moving away from the discharges.

The maximum energy typical capacitors can store is from 3 to 4 kJ. If the circuitry is properly matched to the metal vaporization rate, about 1g of uranium or thorium can be released for each discharge. This circuit matching would of course imply that very little energy is left in the capacitor after the wire has melted. A typical history of the current through and voltage across the terminals holding an exploding wire is shown in Figure 4.3.[4-3]

In order to release more uranimum or thorium vapor using this technique, a system which explodes several wires in sequence may be developed. The limit on t'e total amount of metal vapor released per flight would thus depend on the cycling time between exploding wire pulses, and ultimately on the energy available from the battery system.

In the repetitive pulsing mode, if we assume the capacitor is charged by a 5000 volt battery at a current of 10 amps, the cycling time between exploding wires would be about 0.1 sec. A total of about 10 gm of metal vapor per sec may thus be released through this method.

The system weight for this capacitor and battery combination would be about 50 lbs for the batteries and 50 lbs for the capacitor bank.
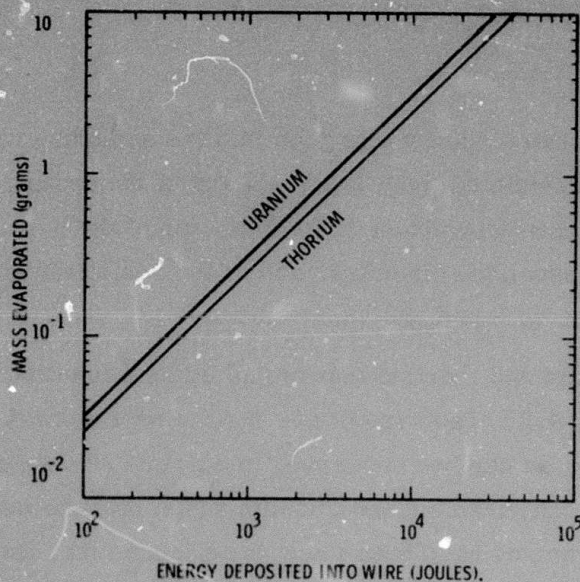
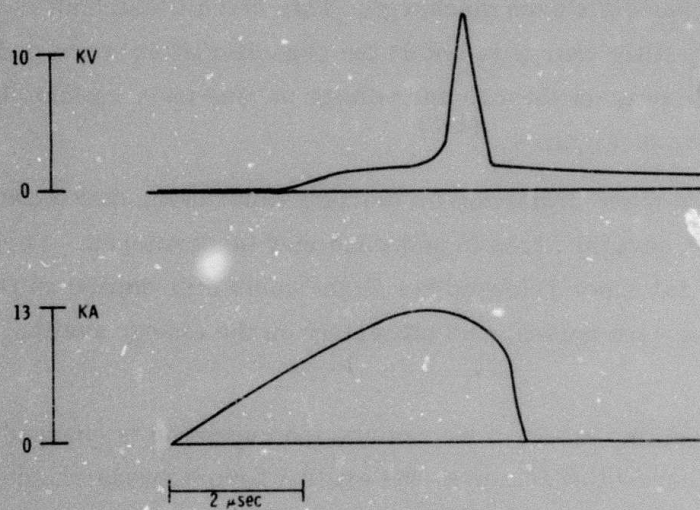Fig. 4.2. Energy Required for Exploding Uranium and Thorium Wires.

Fig. 4.3. Correlated Electrical and Streak Camera
Data for 10-mil Copper Wire.
(v = 3 kV, C = 32 μF).

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5. SOLID CHEMICAL EVAPORATOR

Morton Camac

INTRODUCTION

A novel method for producing high temperatures is under investigation by Macek at Atlantic Research.[5-1] The objective is to produce a reaction between materials which yields high temperatures and reaction products which remain in a condensed state. This allows the hot reaction products to be contained in the original vessel without excessive pressures on the walls. Such a system can be used to produce a source of pure vapors of refractory metals and materials. A schematic design of the system is shown in Fig. 5.1. A cylindrical vessel, about 5 cm in diameter, contains a mixture of tungsten oxide, WO_3, and zircorium, Zr. An ignition wire is along the axis of the cylinder. The mixture is in a thin-walled refractory vessel coated with the material to be evaporated. Possible vessel wall materials are graphite, tantalum, tungsten, or hafnium carbide.

Upon ignition, the mixture undergoes the reaction

$$2WO_3 + 3 Zr \rightarrow 2W + 3ZrO_2 \quad .$$
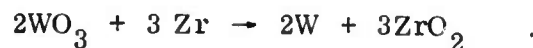
This reaction has two important properties. It produces high temperatures and the reaction products, W and ZnO_2, remain condensed at these high temperatires. The constituents of the system are listed in Table 5-I, assuming a one torr vapor pressure for the gas phase molecules. The table gives the number of moles for each species for a vessel containing 100 grams. The major gaseous species are O, ZrO and ZrO_2. The minor species concentrations shown in the table are very uncertain because the thermodynamic constants are poorly known. The analysis presented in this section
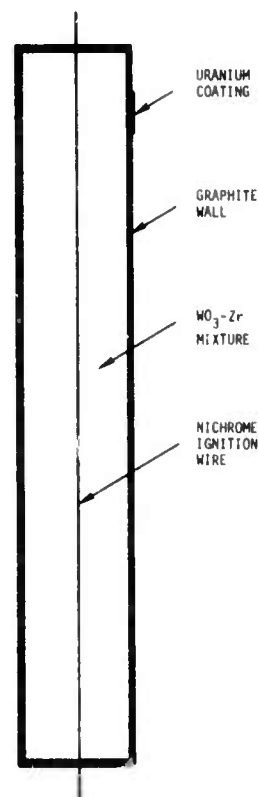

URANIUM COATING

GRAPHITE WALL

WO_3-Zr MIXTURE

NICHROME IGNITION WIRE

Fig. 5.1. Uranium Evaporation by Flashbulb Technique

uses the 3070°K temperature shown in Table 5-I. If the vapor pressure of the gas were higher, then the temperatures would be higher, and the system performance would be better.

TABLE 5-I
EQUILIBRIUM SPECIES CONCENTRATIONS

(Assuming 10^{-3} Atmosphere Vapor Pressure) Temperature = 3070°K								
Species	W	$Zr\,O_2$	$Zr\,O_2$ (g)	$Zr\,O_2$ (g)	O (g)	WO (g)	WO_2 (g)	WO_3 (g)
Moles/100 gr Sample	0.27	9.33	0.037	0.037	0.032	0.0016	0.0015	0.001

In the ideal operation of this device, a very high temperature region is initiated along the axis by the ignition wire. The WO_3-Zr mixture is ignited and a "flame" front propagates radially outward. At the instant the front reaches the surface, it is assumed the whole system, including the wall, is at the same temperature, 3070°K. The heated uranium on the surface proceeds to evaporate. The surface can cool rapidly due to (1) thermal radiation and (2) uranium evaporation. Figure 3.3 shows that thermal radiation cooling dominates up to 3200°K, after which evaporation cooling dominates. Radiation from the surface extracts heat from, and consequently, cools the material below the surface. Figure 5.2 shows the surface cooling time due to radiation cooling as a function of the surface temperature, based on a uranium surface emissivity of 1/3. The time for the temperature to change by 100°K is plotted as a function of surface temperature. We assume the same value of ($\rho C_p k$) for the wall and the W-ZrO_2 mixture; k is the thermal conductivity, ρ is the density, and C_p is specific heat. Curves are shown for ($\rho C_p k$) equal to 1, 0.1 and 0.01 cal^2/sec cm^4-$^O K^2$.
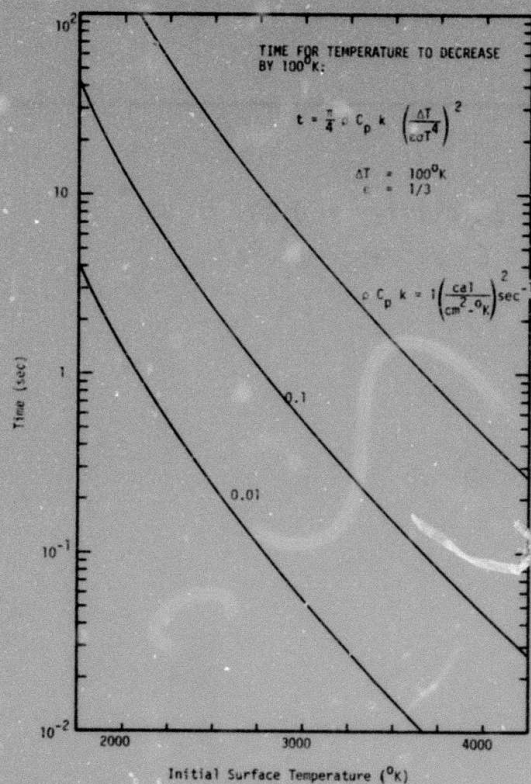
Fig. 5.2. Radiative Cooling of Surface

The amount of uranium evaporated per unit area of surface, $\dot{m}$, is given by the relation

$$\dot{m} = \int_0^\infty E(T)\, dt = \int_{0^\circ K}^\infty E(T)\, \frac{dT}{(dT/dt)} \quad .$$

$E(T)$ is the evaporation rate per unit area and is a strong function of the temperature (see Fig. 3.3). Figure 5.3 shows the uranium evaporation rate as a function of time assuming $C_p k = 0.5$ cal^2/sec-cm^4-$^\circ K^2$. The shaded area under the curve gives a total evaporation in 10 seconds of 120 mg per cm^2 of surface.

The heat conduction is rapid, and in a few seconds the cold front reaches the axis. In 20 sec, the surface temperature has cooled enough so that the uranium evaporation has essentially ceased. A larger diameter vessel would yield more vapor but would add significantly to the overall system weight. The total system weight shown in Fig. 5.1 is approximately 6 kg; the exact weight depending upon the material packing fraction. The ratio of weight of uranium vapor to the total weight of the system is approximately 10^{-3}. Note that a composite of many vessels could be used to furnish a larger source of uranium vapor.
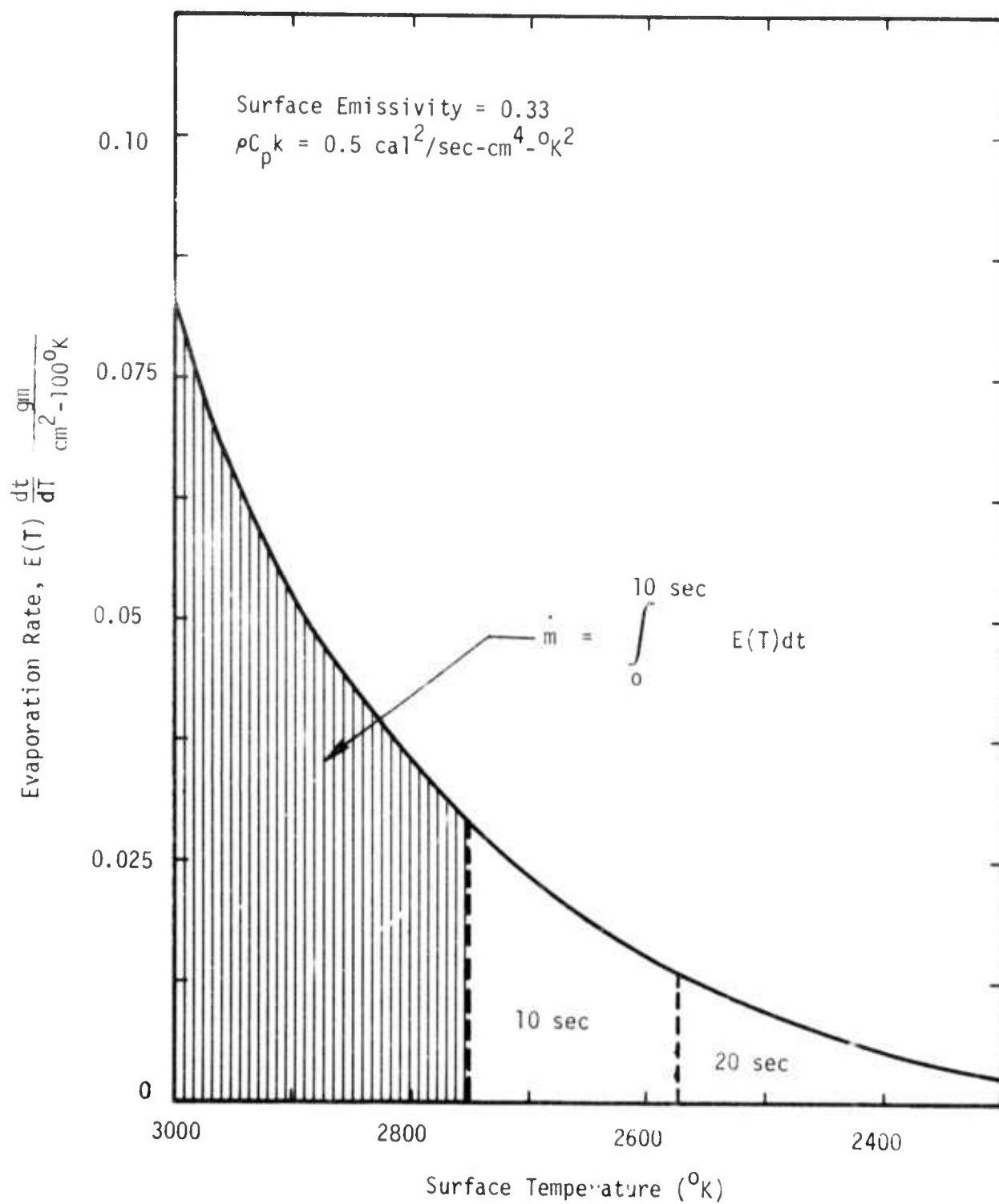
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Fig. 5.3. Uranium Evaporation Rate

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REPORT SUMMARY

Because certain simple uranium and thorium oxides exhibit ionization potentials which are lower than their metal-oxygen bond strengths their low temperature and pressure chemistry can result in the production of stable ionized species. Release of uranium or thorium capor in the presence of ambient atomic and molecular oxygen in the upper atmosphere may result in the formation of stable ionic metal clouds which extend over large volumes. Radar and optical observation of these clouds could yield information about upper atmospheric properties.

This report reviews a number of techniques for the release of U and Th, evaporation by chemical and electrical heating, and exploding wires. These studies are at a feasibility level and are based on literature reviews, calculations of model system's responses and discussions with researches involved in atmospheric release work.

The initial chapter presents the results of a literature search for successfully synthesized volatire compounds of uranium and thorium containing liquids which will be oxidized by ambient upper atmospheric species. The compounds $U(BH_4)_4$ and $U(BH_4)_3 (BH_3CH_3)$ are identified as suitable release chemicals. A number of other possible choices are discussed.

Chapters 2 and 5 present possible themochemical heating schemes which could be utilized to vaporize thin coatings of U and Th while Chapter 3 discusses electrical heating techniques to accomplish this purpose. Various materials considerations and the balance between radiative and evaporative cooling are discussed. Chapter 4 evaluates the technique of using an electrical pulse to evaporatively explode uranium or thorium wires.

Initial uranium and thorium release efforts should utilize the relatively convenient gaseous compounds discussed in Chapter 1. If the results of these initial releases are of sufficient interest development of one or more of the pure vapor release techniques described in Chapters 2 to 5 should be undertaken.

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